

BLANKIT AS A BLEACHING
AGENT IN PAPER MAKING

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ARMOUR INSTITUTE OF TECHNOLOGY

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BLANKIT AS A BLEACHING AGENT

IN PAPER MAKING

A THESIS

Presented by

F. R. SQUAIR

to the

PRESIDENT AND FACULTY.

of

ARMOUR INSTITUTE OF TECHNOLOGY

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Having Completed the Prescribed Course

of Study in

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4

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BLANKIT AS A BLEACHING AGENT

IN PAPER MAKING.

The object of this work is to compare the bleaching effect of "blankit" with that of the other materials ordinarily used for this purpose in the manufacture of paper.

Paper consists of almost pure cellulose fibers felted together to form a sheet. A certain amount of mineral matter is always mixed with the fiber to increase the weight of the paper and to make it smooth and less porous. Most papers, especially those for writing and printing, contain some size, which makes the fibers stick together and gives a coating to the paper which prevents absorption and spreading of the ink. The raw materials used for making the fiber are cotton or linen rags, wood pulp, esparto, jute, flax, straw, hemp, megasse, etc.; a few other materials of like nature may be used, but they are ^{not} as yet of any commercial importance. The minerals used for loading are clay, gypsum, or precipitated calcium sulphate, barium sulphate, calcium carbonate, or ground talc. The size is made from gelatine, or casein for an "animal size".

The raw materials furnishing the fiber are treated in such a way as to remove any incrusting matter and organic substances other than cellulose, and to disintegrate

the cellulose as far as possible into its individual fibers. This is usually done by boiling the material under pressure in a solution of either caustic soda, sulphurous acid or acid sulphite of calcium and magnesium, or milk of lime. The first method is called the soda process, and the second, the sulphite process; milk of lime is used where only slight treatment is necessary, as in the case of rags or old paper.

After thorough boiling the pulp is run into a "hollander" or pulp machine, where it is beaten by revolving knives, which complete the process of disintegration, and form a thin cream of finely subdivided pulp. This pulp is run into tanks where it is bleached; it is then ready to be run over wire screens or gauge to form sheets of paper. After drying the sheets are passed through a gelatin or glue solution; hung up and allowed to dry very slowly. For a printing paper, a rosin size is mixed with the pulp before it is made into sheets, and some alum solution is added to liberate some of the rosin. After being made into sheets, the paper is passed between hot rolls which fuses the rosin and gives to the paper a glossy surface.

Pulp which is bleached with calcium hypochlorite usually has a yellow tinge which is neutralized by adding

a trace of blue such as ultramarine or methylene blue.

The Bleaching of the pulp is a very important step in the process of manufacture, since upon it depends to a great extent the quality and value of the paper. Bleaching powder or a hypochlorite solution is used almost exclusively for this purpose. Other materials such as ozone, hydrogen peroxide, sulphurous acid or liquid chlorine, have been tried, but have only a limited application, owing to their cost or to their deleterious action upon the cellulose fiber.

The bleaching action of chloride of lime is essentially one of oxidation; the lime contributes to the effect by hydrolysing the colored compounds present in the fiber, and by combining with the colorless products of the oxidation. The formula for bleaching powder is $\text{Ca} \begin{smallmatrix} \text{Cl} \\ \text{OCl} \end{smallmatrix}$ when dissolved in water this is hydrolysed to calcium chloride (CaCl_2) and calcium hypochlorite ($\text{Ca}(\text{OCl})_2$). The calcium hypochlorite decomposes slowly into calcium chloride and oxygen. This decomposition, and consequently the bleaching action, is usually accelerated by the addition of a small amount of hydrochloric or sulphuric acid, which converts the calcium hypochlorite into hypochlorous

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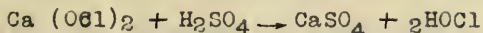
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acid according to the equation:-



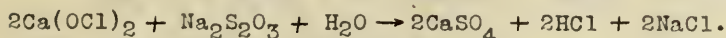
the HOCl decomposing much more rapidly than the Ca (OCl)_2 into hydrochloric acid and oxygen.

The time necessary to produce a perfect bleach with bleaching powder depends on the nature and condition of the pulp, on the degree of concentration of the liquor, and on the temperature at which the operation is conducted. By giving a longer time to the bleaching there is less risk of damage to the fiber and consequently a greater yield of bleached pulp. The amount of bleaching powder for well boiled pulps may be stated approximately as follows:-

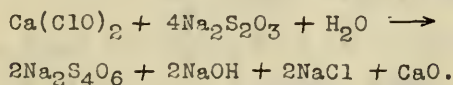
Rags ---	2 - 5%	on weight of the fiber.					
Esparto	7 - 12%	"	"	"	"	"	"
Straw - -	7 - 10%	"	"	"	"	"	"
Wood - -	15 - 20%	"	"	"	"	"	"

As soon as the pulp has been thoroughly bleached, the action should be stopped, especially if the liquor has been heated; otherwise the fiber is liable to be chlorinated, and the color again taken up. The excess of hypochlorite is therefore washed out with water, or if this cannot be done quickly enough, it is destroyed by adding an antichlor such as sodium thiosulphate.

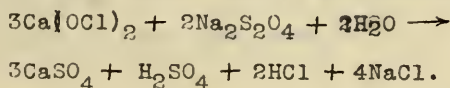
The thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) being a reducing agent combines with the hypochlorite according to the following equation:-



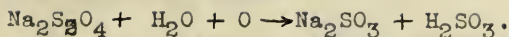
or, in case the solutions are very dilute,



Blankit is sodium hyposulphite ($\text{Na}_2\text{S}_2\text{O}_4$), and is very similar to sodium thiosulphate in its chemical reactions. Its action is always a reducing one, being in this respect just the opposite of hypochlorous acid. In using blankit to bleach pulp, it could not be used along with bleaching powder, since it would act merely as an anti-chlor and neutralize the hypochlorite according to the equation:-



The bleaching effect of blankit depends upon the fact that it combines with the oxygen of the coloring matter of the fiber, the products formed being in most cases colorless or very nearly so. The action of the blankit may be represented as follows:-



The sodium bisulphite then combines with more oxygen:-

$\text{Na}_2\text{SO}_3 + \text{H}_2\text{SO}_3 + 2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$. the final product being sodium bisulphate.

Up to the present blankit has found its largest field in sugar refining, where it is being used successfully as a clarifying and bleaching agent. When used for this purpose it has been found that a very small per cent of blankit is sufficient, and that the reaction occurs almost immediately after its addition. Blankit has recently been given a thorough test as a bleaching agent for toilet soaps, with favorable results. The action in this case was slow, only attaining its maximum effect in two months or more. From the action in the above cases it was thought that blankit might exert a bleaching action on paper pulp which would have advantages over the hypochlorite solutions now used.

The thesis work was arranged in the following manner: pulp was prepared and samples were taken and treated with various amounts of bleaching powder and blankit. The samples were then made up into sheets of paper in the customary way, in order to show as much as possible the effect

of each bleaching agent.

The only material at hand for making pulp, was exhausted sugar cane (megasse), so this was used, although it is not regarded as furnishing fiber for the highest grade paper. In the process of drying the sugar cane the pith is separated from the fiber; for this reason it was decided to use both the pith and the fiber, and to note any differences in the paper made from them.

The pith was used first in making up a pulp. Seven^{tenths}_A pounds of pith was placed in the boiler and thoroughly mixed with 1560 c.c. of 10% caustic soda solution. This corresponds to 49% of caustic soda on the weight of the pith. The boiler was closed securely and heated for 5 hours at a pressure varying between 80 and 120 pounds per square inch. The contents were allowed to cool, and were thoroughly washed and weighed. A sample was taken to determine the per cent of dry pulp present. The analysis showed 6% of dry pulp; the weight of the wet pulp was 2.04 pounds. This makes the yield of dry pulp from dry pith 17.5%, which is much smaller than the average yield of other fiber producing materials.

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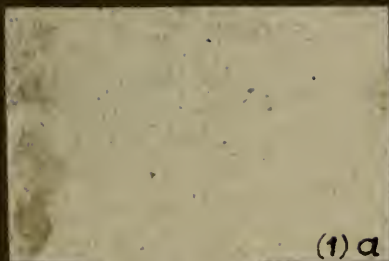
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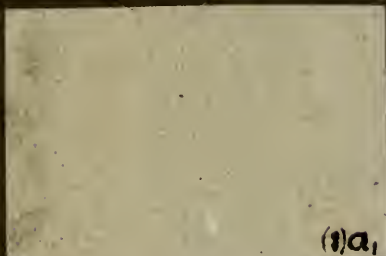
(1)



(1) a



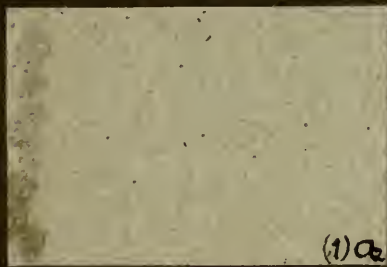
(1) b



(1) a₁



(1) b₁



(1) a₂



(1) C₁

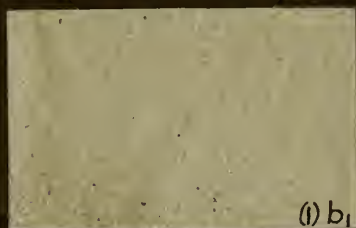
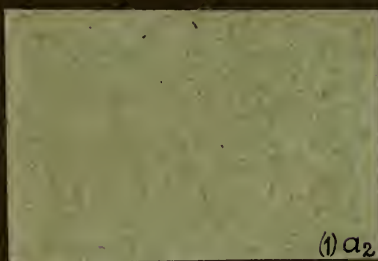
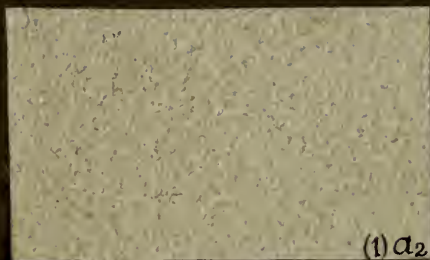


(1) C₂

*Paper prepared
without Rosin.size.*

Eighty-four hundredths pounds of fiber was next used with 1,800 c.c. (47%) of caustic soda; this was heated in the boiler for 7-1/2 hours at a pressure of 85[#] per square inch, and a temperature of 165° C. The weight of wet pulp was 3.38 pounds, the per cent of dry pulp, 5.8%, making the yield 23.3%.

A third run was made with pith, but in place of a solution of 10% caustic soda, a solution of 9% lime and 1% caustic soda was used. This was done simply as an experiment to ascertain whether or not the pith would be sufficiently disintegrated to make a fairly good paper. .58 pounds of pith was mixed with 2,200 c.c. of the above solution, and heated for 6-1/2 hours at a temperature of 156° C. and pressure of 100 to 112 pounds per square inch. Upon examining the mixture it was found that the fibers were still hard and appeared to be only slightly disintegrated. 470 c.c. of 10% caustic soda solution were then added and the boiling continued for 2-1/2 hours. The total time of heating was ^{9 hours.} used. The wet pulp obtained from this run weighed 2.96 pounds and contained 10% of dry pulp, thus giving a yield of 51% of dry pulp. This pulp was coarse and hard





and not subdivided into such fine fibers as were the two previous pulps.

BLEACHING THE PULP.

(1) The pulp obtained from the pith by the first method was used first.

(a) .8 pounds of wet pulp was bleached with 20% of bleaching powder, the resulting color being a dark yellow. This was divided into three parts; the first (a) was kept as a sample, the second(a_1) was treated with 4% of blankit after the hypochlorite solution had been thoroughly washed out; the third part (a_2) after washing, was treated with 25% of blankit. The blankit in each case removed the yellow color and left the pulp a light gray color. Pulp a_2 had a little lighter shade than a_1 , but the difference in shade did not at all correspond to the difference in the amounts of blankit used.

b .22 pounds of wet pulp was bleached with 6.6% of blankit. The yellow tinge was removed and the resulting color was a fairly light gray. (b_1) One half of this pulp was treated with 10% of bleaching powder, after the blankit had been washed out.

c_1 .22 pounds of wet pulp was treated first with 8% of



(2)



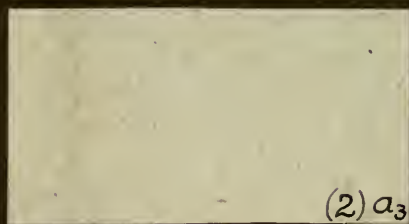
(2) a



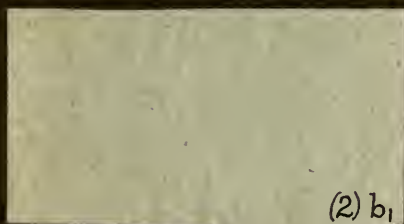
(2) a_2



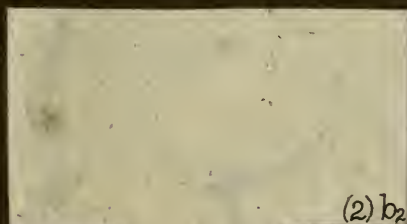
(2) a_1



(2) a_3



(2) b_1



(2) b_2

bleaching powder, and, after washing, with 6.6% of blankit.

c₂ The same amount of pulp as in c₁ was treated with 13% of bleaching powder and 4% of blankit at the same time. The bleaching effect was much less than in a₁, showing that the hypochlorite solution had been weakened by the blankit.

(2)P Samples of the pulp made from the fiber were next treated with varying amounts of bleaching powder and blankit. This pulp was of a much lighter color and finer texture than the pulp made from pith.

The first six samples after being treated with bleaching powder, were thoroughly washed, and then the blankit added. The proportions used may be tabulated as follows:-

Sample	a	a ₁	a ₂	a ₃	b ₁	b ₂
Bleaching Powd. %	12	12	12	12	7	7
Blankit, %		.75	1.35	2.25	1.25	2.5

The action of the blankit in removing the yellow color from the pulp was very noticeable. After adding the blankit in a₁ the color was much lighter; the final color of a₂ and a₃ was slightly grayish.

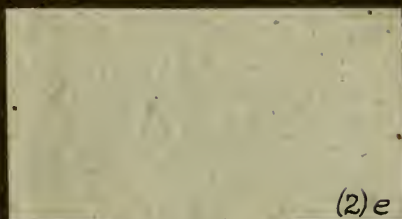
The next four samples were treated with blankit alone, in the following amounts:-



(2)



(2) c



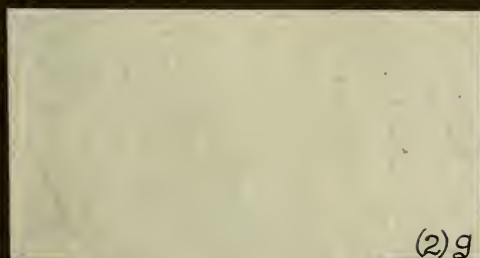
(2) e



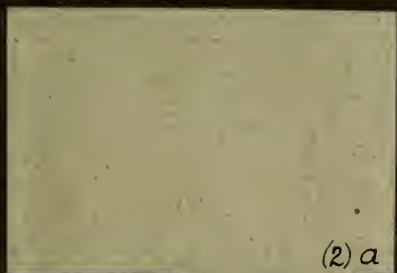
(2) d



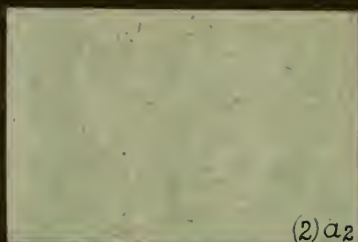
(2) f



(2) g



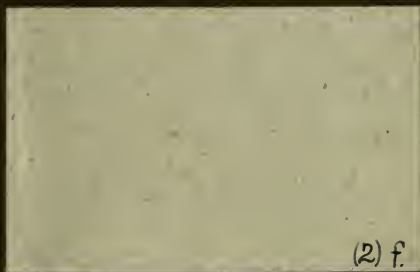
(2) a



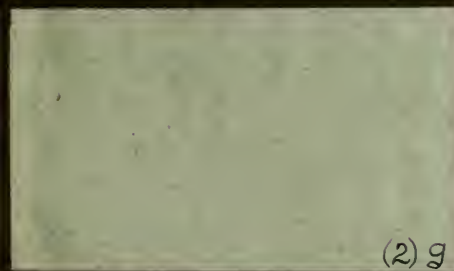
(2) a₂



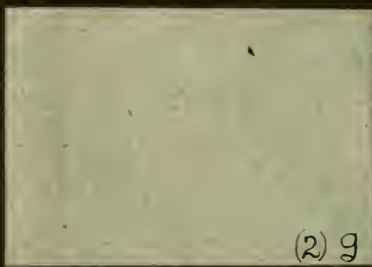
(2) e



(2) f



(2) g



(2) g

Paper colored with
Methylene Blue.

Sample	c.	d.	e.	f.
Blankit, %, .75		1.25	2.5	4%

The time required for obtaining the maximum bleaching effect with bleaching powder was between one hour and one hour and a half, the solution being slightly warmed.

When blankit was added to the cold mixture of pulp, the final color was obtained within half an hour; when added to the hot solution it was reached in 5 or 10 minutes.

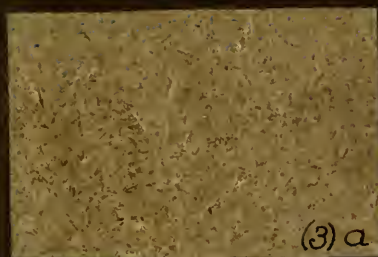
The next sample was bleached with hydrogen peroxide - 40 c.c. to 5.5 grams of pulp. The bleach in this case was complete, the resulting color being practically pure white.

- (3) The third set of samples to be bleached was taken from the pulp with which milk of lime had been used. The first sample, a, when treated with 14% of bleaching powder turned to a reddish brown color. A part, a_1 of this was taken and 8% of blankit added to it; the resulting color was a light green.

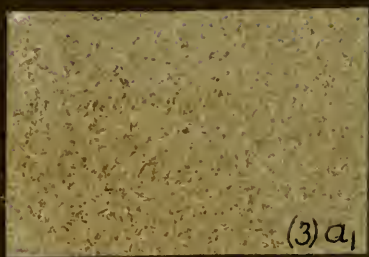
Three other samples of pulp were taken for bleaching with blankit alone; 1-1/2% of blankit was added to the first, b_1 , 3% to the second, b_2 , and 5% to the third b_3 . The color of the pulp was made a little lighter in each case, but the resulting colors of all three were practically



(3) c



(3) a



(3) a₁



(3) b₁



(3) b₃

the same, so that only the first and third were made up into paper.

The last sample, c, was bleached with hydrogen-peroxide. Here, as in the previous case, the color obtained was very light. The proportions used were 45 c.c. of hydrogen peroxide to 7 grams of dry pulp.

The next part of the work was to make up the different samples of bleached pulp into paper in such a way as to show to the best advantage the comparison between the various bleach effects. To do this each sample was treated exactly the same as every other sample. Only a small amount of filler, 10%, was used, for fear it might hide some of the color due to the bleaching.

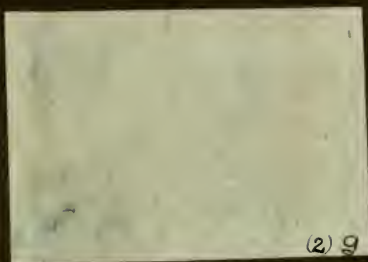
A rosin size was used and was prepared by boiling 50 grams of rosinⁱⁿ 233 c.c. of a 3.0 % solution of sodium carbonate, until the rosin was completely dissolved or saponified. This gave about a 25% solution of rosin soap. Approximately 8% of size was mixed with the pulp, which was then diluted with water until it formed a thin cream. This cream after being thoroughly stirred, was run evenly over wire cloth stretched on a frame. As the water drained off, the screen was moved back and forth to make the

fibers felt and thus strengthen the paper. If the sheet was removed from the screen before it was dry, it would shrink out of shape on drying; the sheet was therefore left on the screen until dry. A hot iron was then used to give a smooth and glossy finish to the paper.

Some samples of the first pulp were made up without any rosin size, and therefore absorb water very rapidly. Some of the sheets of the second (fiber) pulp were dipped in gelatine to give to the paper if possible a better surface. It will be noticed that the sheets of paper contain many black or brown specks; these are particles of dirt that got mixed with the cane while it was exposed in the laboratory, and they could not be removed. The fibers of the third pulp were so coarse that they matted together with difficulty; about 15% of rosin size was used, and even after this large amount of size, the sheets hung together so poorly, that they had to be dipped in a glue or gelatine solution and then dried.

To several samples of the bleached pulp from the fiber were added a few drops of a 3% solution of methylene blue.

Sample	a	a ₂	b ₂	e	f	g	g
Drops:	2	3	2	2	12	3	12



(2) 9



(2) b₁



(2) b₁

(2) b₁, with various amounts of
Methylene Blue.

(2) b₁

It was noticed that the pulp bleached with hypochlorite was lightened considerably by the color, while the blankit bleached pulp was unaffected by even comparatively large amounts of the blue solution. This would seem to indicate that the pulp bleached with blankit might be lightened by a pink or yellow, instead of a blue solution.

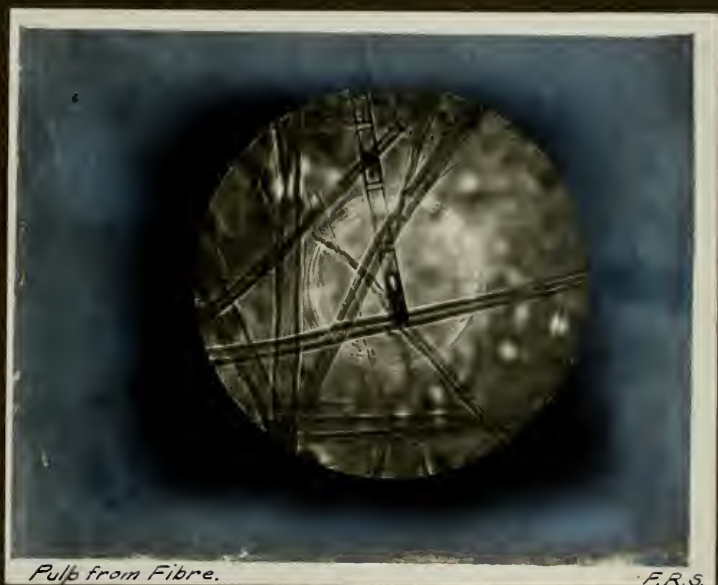
It was found that practically no advantage was gained by using more than 2% of blankit; when more than this was used a more distinct gray color was the result. The best bleach effect obtained by the use of blankit above did not appear to be as good as the color obtained with 15% of bleaching powder. The difference in price, however, must be taken into consideration, when a comparison of the two bleaching reagents is to be made. The cost of bleaching powder per pound is; . The cost of blankit per pound, . When it is unnecessary for the pulp to be bleached to a pure white, it is evident that in this case the use of blankit would be advantageous. It is quite possible that with pulp made from material other than megasse, the blankit bleach might reach a lighter color than in the present case.

In order to show clearly any difference that might exist between the pulp made from pith and that made from fiber, several microscopic slides of the two pulps were prepared. Microscopic photographs of the pulp magnified 1200 times were then taken, and are shown herewith. It will be seen that the pulp from the fiber consists of thin and fairly homogeneous fibers. The pulp from the pith has also some fibers, but these are some that passed thru the sieve, when the pith was being separated from the fiber. This slide also contains numerous flat looking sheets of cellulose which would probably not have as good felting qualities as pulp composed of fine threads. The pulp made up with milk of lime appeared under the microscope to be composed of short thick fibers, which were themselves bundles of small threads, that had been only partly dissociated.



Pulp from Pith.

F.R.S.



Pulp from Fibre.

F.R.S.







